PART ONE
NEGATIVELY SUBSTITUTED MESITYLENE DERIVATIVES

PART TWO
VINYL PERESTERS

BY

ELMER ROY TRUMBULL, JR.

A.B., Dartmouth College, 1944

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

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PART ONE

NEGATIVELY SUBSTITUTED MESITYLENE DERIVATIVES

Introduction

A number of stable enol derivatives of diaryl acetaldehydes such as 2-mesityl-2-phenylvinyl alcohol have recently been prepared (1,2). The necessary and sufficient requirement for the stability of such enols is the presence of one group which possesses unusual blocking power such as the mesityl radical. In many instances the introduction of negative groups in the mesitylene nucleus has been found to decrease the amount of hindrance which this nucleus presents (3,4). This investigation is concerned with a search for useful methods of preparation of derivatives of 2-mesityl-2-phenylvinyl alcohol having negative substituents on the mesityl ring, for the purpose of examining the stability of such molecules.

Discussion of Results

2-Bromomesityl-2-phenylvinyl alcohol as prepared by Maynert (2) was found to possess a wide and variable melting range. That this was not due to a ready interconversion of the vinyl alcohol and the corresponding aldehyde was demonstrated by hydrolysis of bromomesitylphenylvinyl acetate to give a sample of vinyl alcohol melting at 110-111°. However this alcohol was shown to be more easily ketonized than mesitylphenylvinyl alcohol by the preparation of a semicarbazone which was formed in a shorter time and in higher yield from the bromo substituted alcohol than from the parent compound.

The synthesis of 2-dibromomesityl-2-phenylvinyl alcohol, which has been attempted by various methods (1,2), was undertaken. Dibromomesitylglycolic acid could not be caused

to condense with benzene, but did react with toluene to form dibromomesityl-*p*-tolylacetic acid. The sodium salt of this acid apparently is capable of existence in a non-polar form. The acid was converted to the corresponding ketene with considerable difficulty, but this product was not reduced by *t*-butylmagnesium chloride.

Several methods for the preparation of 3-cyanomesitylphenylacetic acid were explored. Mesitonitrile could not be caused to condense with mandelic acid. 3-Cyanoacetomesitylene was prepared by a Rosenmund-von Braun reaction using bromoacetomesitylene and was oxidized to the corresponding glyoxal. When this product was heated with alkali to bring about rearrangement to cyanomesitylglycolic acid, the nitrile group was also attacked, being converted to an amide. Since no conditions could be found whereby the rearrangement could be effected without hydrolysis, this scheme was abandoned. An attempt to prepare the desired acid by a Rosenmund-von Braun reaction with 3-bromomesitylphenylacetic acid itself led to the formation of 3-cyano-2,4,6-trimethyldiphenylmethane, presumably due to decarboxylation during the reaction.

The preparation of a vinyl alcohol by dehydration of a properly substituted diol was explored in an attempt to discover a synthesis of 3-nitromesitylphenylvinyl alcohol. 1-Mesityl - 2 - phenylethane-1,2-diacetate was nitrated and hydrolyzed to yield 1-(3-nitromesityl)-2-phenylethane-1,2-diol. This compound could not be dehydrated to the vinyl alcohol with either hydrochloric or sulfuric acid.

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PART TWO

VINYL PERESTERS

Introduction

The action of lead tetraacetate on 2,2-dimesitylvinyl alcohol gave rise to a new compound whose difference from the parent substance corresponded to the introduction of an acetoxyl group in place of a hydrogen atom (1). The observation that this product was hydrolyzed by ethylmagnesium bromide to the original vinyl alcohol (2) indicated that the hydrogen atom of the hydroxyl group was the one which was replaced and the new product was most likely 2,2-dimesitylvinyl peracetate. Since the formation of a perester directly from an alcohol was without precedent (3), an investigation of the action of lead tetraacetate on various alcohols and stable enols was undertaken.

Discussion of Results

The action of lead tetraacetate on mesitylphenylvinyl alcohol led to the formation of a new compound analogous to that obtained from dimesitylvinyl alcohol. That this product was not aceto-mesitylphenylacetic anhydride, which would be formed by the replacement of the vinyl hydrogen atom by an acetoxyl radical, was proved by the synthesis of this anhydride. The hydrolysis of mesitylphenylvinyl peracetate was effected in several ways which are discussed in three groups.

1. Alkaline Media . . . . Hydrolysis of the peracetate in alcoholic potassium hydroxide led to the formation of 2,4,6-trimethylbenzoin. Under the conditions of the experiment, part of this product was oxidized to the benzil. In the presence of sodium ethoxide a certain amount of mesitoic acid, which is formed by cleavage of the diketone, was also isolated.

2. Acid Media . . . . Alcoholic hydrogen chloride gave a

much cleaner hydrolysis, the only product isolated being ethyl mesitylphenylacetate. In the presence of dilute alcohol a mixture of mesitylphenylacetic acid and its ethyl ester was obtained.

3. Grignard Reagents . . . . With ethyl- or phenylmagnesium bromide the main product was an oil which has not been identified. In addition a small amount of mesitylphenylvinyl alcohol was isolated from the reaction with ethylmagnesium bromide. By hydrolysis of the peracetate with isobutylmagnesium bromide, a new product was obtained which is apparently the *cis*- isomer of the known mesitylphenylvinyl alcohol. This compound was characterized by the preparation of an acetate and a benzoate which differed from the known derivatives.

These products have been explained on the basis of a mechanism which assumes that the peracetate is hydrolyzed initially to a hydroperoxide which then rearranges or is reduced.

The formation of peracetates seems to be characteristic of diarylvinyl alcohols. These derivatives have been prepared from mesitylphenyl-, dimesityl-, bromomesitylphenyl-, isodurylphenyl-, and mesityl-*p*-tolylvinyl alcohol. Only in the case of mesitylphenylvinyl peracetate was a new isomer of the vinyl alcohol obtained by hydrolysis.

Other hydroxyl-bearing molecules with which the reaction was tried did not yield the peracetate derivatives. Triphenylcarbinol was recovered unchanged; 2,2-dimesityl-1-phenylvinyl alcohol and phenol were converted to tars; 2,2′,4,4′,6,6′-hexaethylstilbenediol was oxidized to the benzil; and desoxymesitoin was converted to a compound which has not been identified but which is not the peracetate.

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VITA

The author was born in Lawrence, Massachusetts, on April 5, 1924. He attended the public schools of that city and was graduated from the Lawrence High School in 1941. In the fall of that year he entered Dartmouth College at Hanover, N. H., whence he received the degree of Bachelor of Arts in October, 1944. The same month he entered the Graduate School of the University of Illinois where he held a teaching assistantship through the summer of 1945. During the next two semesters he held a research assistantship sponsored by the Rohm and Haas Company. He held a University Fellowship from June, 1946, to September, 1946, and a duPont Fellowship from October, 1946, through May, 1947.

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